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Studies on Synthesis and Dielectric Properties of Rare Earth Doped Pottasium Based Double Molybdates

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ABSTRACT

The alkali molybdate doped with different rare earth ions having general formula $KRE(XO_4)_2$ (where RE = Sm or Eu) were prepared by high temperature solid state reaction method. The XRD data show the formation of a single phase materials for both the compositions with orthorhombic unit cell. The variation of dielectric parameters as a function of frequency and temperature reveal interesting properties of these compositions. The concept of impedance analysis along with the strength of procedure in analyzing dielectric property of material have makes it easier to separate out the contribution due to different types of electrical conduction phenomena occurring in these materials. In addition, the real and the imaginary parts of the total impedance are plotted as a function of frequency to reveal the true picture of material properties. Complex plane impedance spectroscopy is also used to explain the observed dielectric behavior of these materials. Temperature dependence of real (ε') and imaginary (ε'') part of dielectric permittivity shows a thermally stable dielectric behavior. Frequency dependence of real part of dielectric constant and dielectric loss curve shows dispersion in these values at all temperature of measurements for both the compositions.

Keywords: Molybdates, Tungsten bronze structure, Rare earth doping, Dielectric properties.

1. INTRODUCTION

The family of important ferroelectrics based on oxygen octahedral form four structural groups namely (i) perovskite structure (ii) bismuth layer structure (iii) lithium niobatestructure and (iv) tungsten bronze structure depending on

network of corner linked oxygen octahedral and its spatial distribution. Numerous molybdates and tungstates with complex doped with trivalent lanthanide and transition-metal activators have played an important role in quantum electronics for more than three decades. The structural diversity in these crystals reflects in a wide variety of physical properties. The tungsten bronze structure consists of framework of BO_6 octahedra where B is commonly occupied by Mo, W, Ta, Nb, Ti ions. The BO_6octahedra share corners in such a way that three types of interstitials are formed. In this structure, each unit cell contains two pentagonal (A) sites coordinated by fifteen oxygen ions, four smaller tetragonal(B) sites coordinated by 12 oxygen ions and four comparatively smallest trigonal(C) sites[1]. Intungsten bronze structure, pentagonal A and tetragonal B sites can accommodate a large number of different cations. This provides a scope for wide varieties of substitutions facilitating a large number of compounds and solid solutions that crystallizes in tungsten bronze structure. Rare-earth molybdates have been executively studied due to their diversity and excellent chemical stability[2,8]. The past years witnessed an increasing interest in the synthesis and characterization of alkali metal rare-earth double molybdates crystals for their intriguing potential properties (magnetism, electricity, optics), as well as a wide variety of applications in industry, military and medical treatment[3,4,5]. Double molybdates with general formula $MRE(XO_4)_2$ (where M = monovalent ion, RE = rare earth ion and X = Mo or W) are recently attracted attention both as a stimulated Raman shifter and as rare earth doped laser hosts[1]. Some members of this series have been studied as a function of their structure for luminescence properties without adding a luminescent ion[6,7,8].

The crystal Structure of some molybdenum oxides have not been solved yet. Hence the characterization of these oxides seems to be an important task understandsthe nature of these materials. Considering the importance of these materials as a ferroelectric and luminescent materials, it is planned to synthesized a system with general formula $NaRE(MoO_4)_2$ (where RE = Sm or Eu) using conventional solid state ceramic method to study their structure and dielectric properties.

The synthesis of this alkali oxo-metallates of the transition metals is quite complex. At first the alkali metals are prepared and they are converted to oxides, peroxides or hyper-oxides by reacting them with molecular oxygen. All the work procedures are accomplished in the inert gas atmosphere. The whole process is tedious and so in this work attempts have been made to adopt a new technique to synthesize molybdates using high temperature solid state reaction method. This method is easy as the starting materials are handled at room temperature innormal atmosphere. In this work, samples are prepared by using high temperature solid state reaction methodto see the effect of different rare earth ions doped materialsand to study the structural properties and dielectric response as the function of frequency and temperature. Ferroelectric materials using solid state reaction route owing to the fact that electrical properties in ferroelectric materials are highly influenced by the microstructure properties of the material such as impurity,

grain size, grain boundaries which in turn are tailored by processing parameters such as calcinations, sintering temperature, heating/cooling rate, sintering atmosphere etc[9,10,11,12].

2. EXPERIMENTAL DETAILS

The $KSm(MoO_4)_2$ and $KSm(MoO_4)_2$ samples were synthesized by conventional high temperature solid state ceramic method. Appropriate amounts of starting materials K_2CO_3, Sm_2O_3 and MoO3 for $KSm(MoO_4)_2$ and K_2CO_3, Eu_2O_3 and MoO_3 for $KEu(MoO_4)_2$ were intimately mixed in an agate mortar using acetone as mixing in an agate mortar. The mixed powders were calcined at 950 °C for two hours. These calcined masses were again mixed and grinded for two hours and pressed as a cylindrical pellet under an isostatic pressure using hydraulic press. These pellets were sintered in alumina crucible at 1050 °C for 02 hours and then furnace cooled to room temperature. The impedance measurements were carried out, on polished and painted with silver paste on both sides, using a computer controlled HIOKI 352-50 LCR Hi-tester as a function of frequency at few selected temperature. The temperature of furnace was accurate upto $\pm 1^0$C. The dielectric and impedance parameter were observed in the parallel plate geometry and C_p, D, Z and Θ parameters were measured in the frequency range 100 Hz-1MHz from room temperature up to 125 ^{0}C, where Cp is parallel plate capacitor in pF, D is dissipation factor or tangent loss (D), Z is the complex impedance and Θ is the phase angle. From these parameters the real part of dielectric constant is calculated as $\varepsilon' = Cp .d/\varepsilon.A$, where C_p is in pF, d is the thickness of the pellet in meter, $\varepsilon_0 = 8.854\times10^{-12}$ F/m is the permittivity of free space and A is the area of pellet in meter^3. Imaginary part of dielectric constant, $\varepsilon'' = \varepsilon'.\tan\delta$. Similarly the real and imaginary parts of total electrical impedance are calculated using relations: $Z' = Z\cos\Theta$ and $Z'' = Z\sin\Theta$. X-ray powder diffraction patterns of sintered pellet were obtained using Rigaku X-ray diffractometer with Cu-Kα λ=1.54Å radiation in the 2Θ range 20^0-60^0.

3. RESULTS AND DISCUSSION

Structural Characterization

The theoretical densities of synthesized and sintered pellets were calculated using XRD data and experimental density using conventional Archimedes principle. The calculated densities for both Sm and Eu doped materials are 3.998 gm/cm^3 and 2.508 gm/cm^3 whereas the experimentally measured densities for the sintered pellets are2.965 gm/cm^3 and 1.938 gm/cm^3 respectively. The percentage density obtained for samplessynthesized in this work are 74 % for Sm doped and 65 % for Eu doped samples. Thus, the prepared samples are highly porous materials. This porosity can be reduced by increasing sintering temperature and sintering time.

The X-ray diffraction analysis was carried out on the sintered pellets of $KSm(MoO_4)_2$ and $KEu(MoO_4)_2$ at room temperature are shown in Figure-1 and Figure-2.The XRD patterns of both the samples indicate the formation of single phase materials. All the observed reflection peaks were indexed using standard computer package POWD MULT. The orthorhombic unit cell was selected as the major phase on

the basis of good agreement between observed and calculated d-values. A careful analysis of both the structures shows that Eu doping slightly distorts the structure from original hexagonal one, whereas Sm doping stabilizes it in more rhombic structure. The difference may lie in electronic structure of the two ions and their orbital coupling with each other.

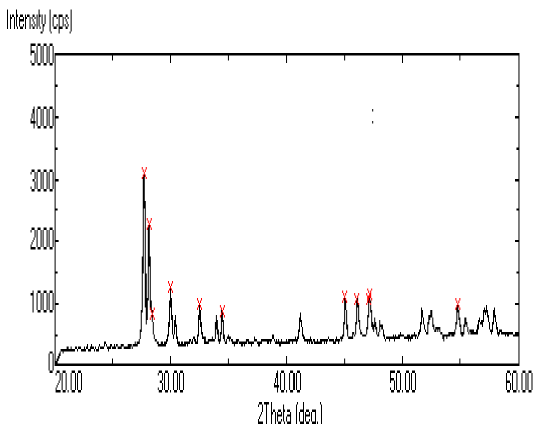

Figure 1. X-ray diffraction pattern of sintered sample of $KSm(MoO_4)_2$

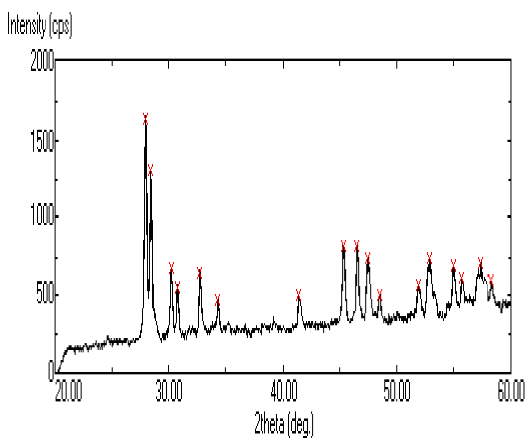

Figure- 2. X-ray diffraction pattern of sintered sample of $KEu(MoO_4)_2$

Dielectric Studies: Effect of Rare Earth Doping

The variation of real part of dielectric constant measured as a function of temperature at few selected frequencies range for Sm doped are shown in figure-1.

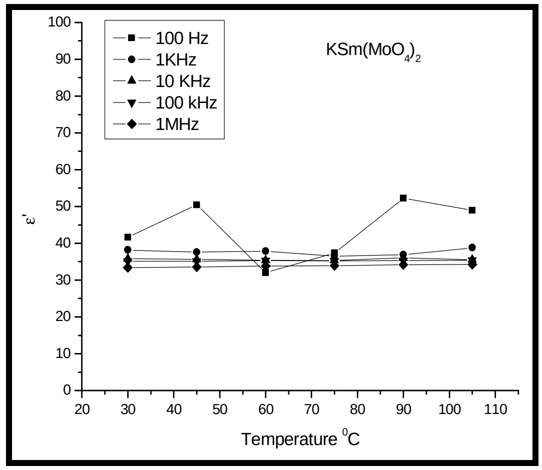

Figure 3: Variation of real part of dielectric constant as a function of temperature for Sm doped samples

The sample show low value of dielectric constant which is almost temperature independent. Further, the dielectric constant and dielectric loss is almost temperature independent except for low frequencies where it shows some dispersion in values. Relatively low value of loss and moderate value of dielectric constant suggest that material may be useful for capacitor applications specially for sensing purpose. The undoped sample K_2MoO_4 show other high value of dielectric constant in comparison to the doped sample. The suppression of dielectric constant and its being temperature independent indicate that doping rare earth increase the disorder in the

material and thus increasing ionic conductivity. The similar results for the Eu doped materials are shown in figure-3 figure-4. In this case, the behavior is slightly different than the Sm doping. Here both the dielectric constant and dielectric loss increase with increasing the temperature. This increase in dielectric response may be due to the interfacial polarization dominating over dipolar polarization and also that ionic conduction dominating at high temperature. The frequency dependence of real part of dielectric constant and frequency dependence of dielectric loss at three different temperatures for both compositions are shown in figure-5–8.

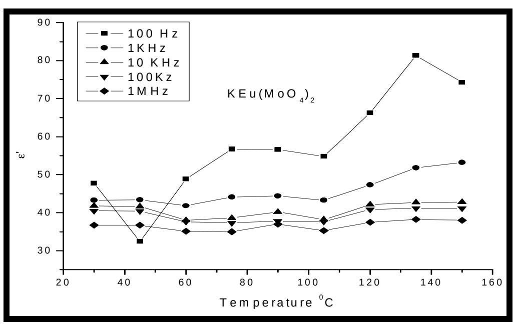

Figure-4: Variation of real part of dielectric constant as a function of temperature for Eu doped samples.

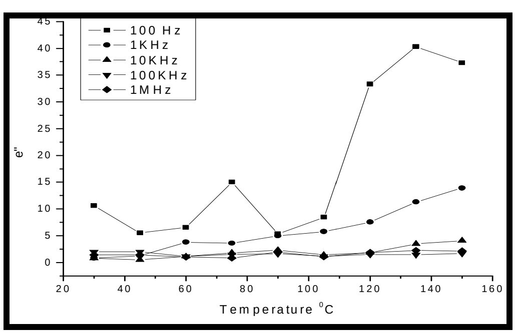

Figure-5: Variation of imaginary part of dielectric constant as a function of temperature for Eu doped samples

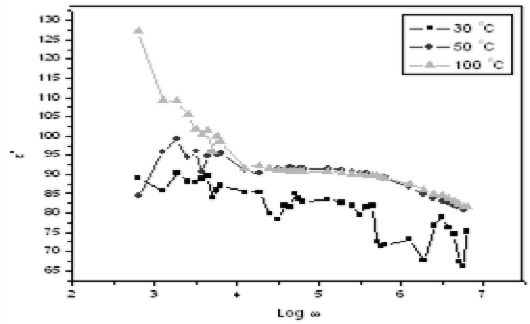

Figure-6: Frequency dependence of real part of dielectric constant for $KSm(MoO_4)_2$ at different temperature.

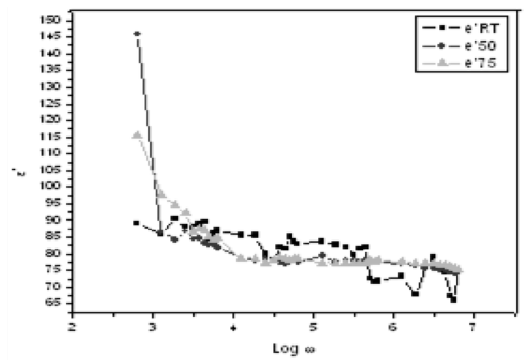

Figure-7: Frequency dependence of real part of dielectric constant for $KEu(MoO_4)_2$ at different temperature

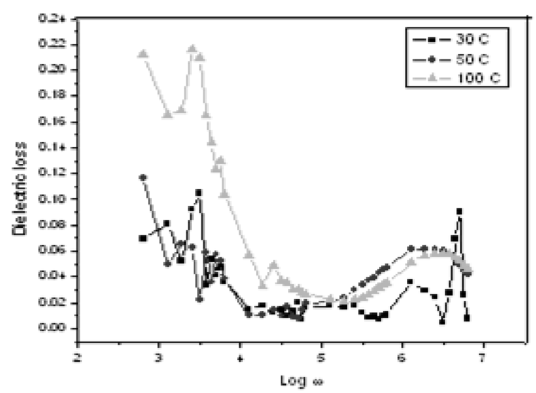

Fig-8: Frequency dependence of dielectric loss for $KSm(MoO_4)_2$ at different temperature

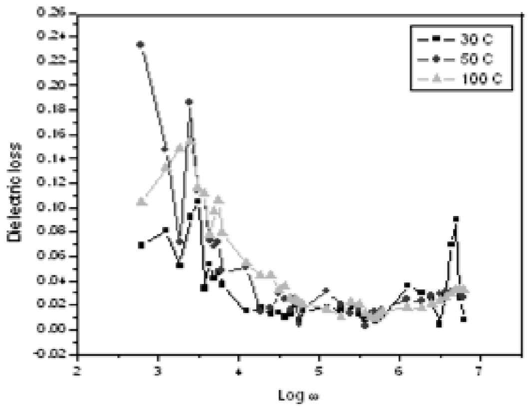

Fig-9: Frequency dependence of dielectric loss for $KEu(MoO_4)_2$ at different temperature

The dielectric constant shows almost no dispersion in the case of Sm doped sample whereas some low frequency dispersion is observed in the case of Eu doped samples. The dielectric loss shows both peak in Sm and Eu doped sample in kHz range. The loss peaks in kHz range are associated with appreciable ionic conductivity and preferably referred as low frequency dielectric dispersion. The behavior would be qualitative explained in accordance with the Johnson power loss.

Impedance studies

In order to understand the nature of material response and the processes involved, impedance spectroscopy analysis is used. Since the secompositions are sintered at relatively low temperature, the presence of large number of oxygen vacancy is not expected. Therefore the dominating impurity may be due to doping ion hopping motion. At low temperature the impedance should be more or less Debye type that is major contribution in resistivity should come out from range. The variation of real and imaginary parts of impedance with frequency is shown in figure -10 and figure-11.

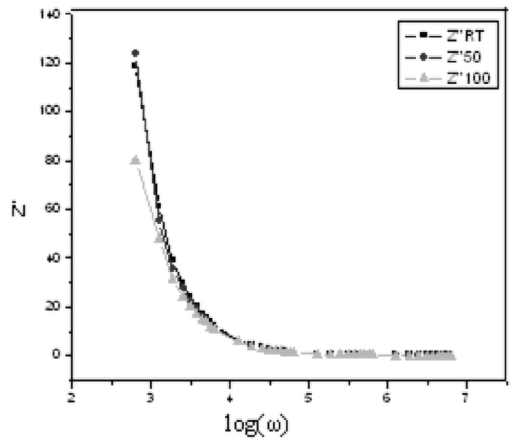

Figure-10:Frequency dependence of the real part of impedance for $KSm(MoO_4)_2$ at different temperature

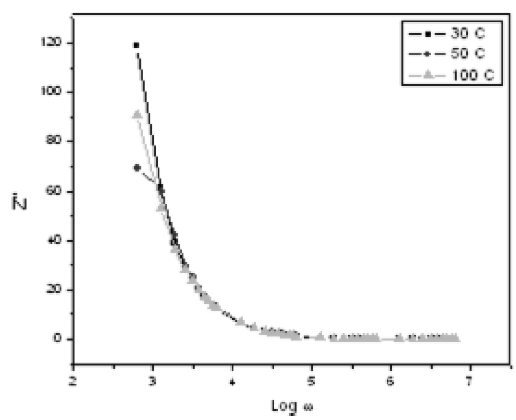

Figure-11: Frequency dependence of imaginary part of impedance for for$KEu(MoO_4)_2$ at different temperature

The impedance decrease exponentially as function of frequency at low frequency and then saturate out at around 10-15 kHz. Further as the temperature increase impedance starts falling from lower value suggesting that the

material resistance decreases as temperature increases. Relatively low value saturation frequency (the frequency were impedance become frequency independent)indicates that heavier ion/dipole may be associated with some switching.

Thus, the impedance analysis at least indicate that the processes occurring these materials have single relaxation and significant amount of A site disordering is not occurring in these compounds. These results are correlated with the fact that crystal structure stabilize is orthorhombicrather than a hexagonal structure. Thus, substituting rare earth ions on A site indicates some interaction among rare earth impurity and A-ion motion resulting in modified structural and dielectric behavior of materials.

4. REFERENCES

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